# PCT

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(54) Title: HYDROPHOBIC, CRYSTALLINE, MICROPOROUS SILACEOUS MATERIALS OF REGULAR GEOMETRY

(57) Abstract

New family of crystalline, microporous silaceous materials of regular geometry, which are substantially hydrophobic, and methods for their preparation. Being resistant to water sorption these materials avoid poisoning and occlusion. These minerals typically have the unit cell structure: $Na_6[(AlO_2)_6(SiO_2)_{30}] \cdot 24H_2O$.

DERIVATIZATION OF TECTOSILICATES

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# HYDROPHOBIC, CRYSTALLINE, MICROPOROUS
# SILACEOUS MATERIALS OF REGULAR GEOMETRY

Crystalline, hydrated aluminous tectosilicates of Group
5   I and Group II elements such as potassium, sodium,
magnesium and calcium are formed in nature or may be
synthesized in the laboratory, and higher polyvalent
ions such as the rare earths are readily introduced by
cation exchange.  Structurally, these tectosilicates are
10  aluminous "framework" silicates which are based on an
infinitely extending three-dimensional network of AlO4
and SiO4 tetrahedra which link to each other by sharing
oxygen ions.  Such frameworks or lattices bear net
negative charges and may be schematically represented by
15  the general structural formula:

$$\left[ \begin{array}{c} O \diagdown \underset{Al^-}{} \diagup O \diagdown \underset{Si}{} \diagup O \diagdown \underset{Si}{} \diagup O \diagdown \underset{Al^-}{} \diagup O \end{array} \right] (M+)m$$
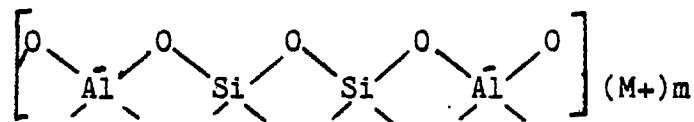
wherein M+ is a cation such as sodium or potassium and m
is equal to the number of negatively-charged aluminum
20  ions within the lattice.  The aluminous tectosilicates
may also be represented by the empirical unit cell
formula:

$$M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot wH_2O$$
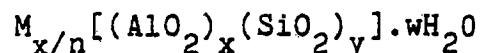
wherein M is the cation of valence n, w is the number of
25  water molecules and the ratio y/x usually is about 1-10,

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depending on the structure of the particular
tectosilicate involved. The sum $(x + y)$ is the total
number of tetrahedra in the unit cell; the portion
within the brackets represents the framework composition
5  of the tectosilicate.

After dehydration, some tectosilicates exhibit large
internal surface areas which are available to absorb
liquids or gases due to the clearing of the channels and
pores, which channels uniformly penetrate the entire
10  volume of the solid. The external surface of a
tectosilicate represents only a small portion of its
total available surface area. Therefore, a dehydrated
tectosilicate will selectively sorb or reject different
molecules on the basis of their effective molecular
15  sizes and shapes. This size-selective sorption action
may be total or partial. If total, the diffusion of one
species into the solid may be wholly prevented while the
diffusion of a second species occurs. If partial, the
components of a binary mixture may diffuse into the
20  solid at different rates, depending on the exposure
conditions involved.

Due to the point electric charges on the surfaces of
aluminous tectosilicate pores, highly polar molecules
such as water, ammonia, alcohols and the like are
25  generally more strongly sorbed than molecules of lower
polarity such as hydrocarbons or inert gasses. Water is
readily sorbed and tightly bound by aluminous
tectosilicates. The water molecules have a strong
tendency to cluster in fragments of a diamond-like
30  lattice both in the liquid and in the vapor phase. This
hydrophilicity has been exploited to remove water in
either the liquid or vapor phase from mixtures of water
and molecules such as the hydrocarbons processed by the
petroleum industry. Gas streams comprising small
35  readily- sorbed gas molecules such as nitrogen, hydrogen

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and the like may also be dried with dehydrated
tectosilicates due to the tectosilicates' extremely
strong attraction for water.

However, aluminous tectosilicate hydrophilicity has
5    prevented the use of these materials to remove
selectively less polar substances from mixtures
containing water.  For example, a tectosilicate which
would remove significant quantities of dissolved ammonia
from human excreta would find utility in a diaper or bed
10   pad where it would act, at least in part, to prevent
ammonia burn and thus to prevent ammonia dermatitis
(diaper rash).  Such materials would also be useful as a
component in litter such as that used to sorb the
excreta of farm animals or household pets.  Although
15   both naturally-occurring and synthetic tectosilicates
have been used to remove nitrogenous components from
liquid human and animal wastes through ion exchange, the
problem of removing dissolved ammonia in the presence of
large amounts of water has not been solved.  See
20   Burholder, U.S. Pat. No. 3,935,363.  The preferential
sorption of water molecules over the ammonia molecules
quickly reduces the tectosilicates' ability to sorb
ammonia.

The desirability of using tectosilicates as sorbents to
25   remove carbon monoxide from tobacco smoke while
permitting larger, flavor-imparting molecules to remain
in the smoke has long been recognized.  However, the
realization of this goal has been effectively thwarted
by the preferential sorption of water vapor which is
30   also a component of tobacco smoke and which rapidly
fills the tectosilicate pores, thereby preventing the
sorption of significant amounts of carbon monoxide.  One
attempt to prevent this occlusion involves the use of a
water-absorbing substance placed in the smoke stream
35   upstream from the tectosilicate, as disclosed in U.S.

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Patent No. 3,658,069. Metal catalysts have also been
introduced into tectosilicates, for example, to oxidize
carbon monoxide to carbon dioxide or to  catalyze the
hydrogenation and cracking of petroleum feedstocks.
5   Such catalyst-supporting tectosilicates are also
susceptible to deactivation by water through pore
occulsion and catalyst poisoning, for example, see
British Pat. No. 2,013,476A.

A tectosilicate material of hydrophobic character would
10  overcome these poisoning and occlusion problems by being
resistant to water sorption while otherwise maintaining
affinity and activity for other molecular species.  Such
hydrophobic tectosilicates would be useful to remove
inpurities from aqueous feedstocks as well as to protect
15  introduced catalysts from deactivation by water.

Accordingly, it is an object of the present invention to
provide a hydrophobic tectosilicate-based material which
resists water sorption while retaining a useful affinity
for other molecules.

20  It is another object of the present invention to provide
a hydrophobic tectosilicate-based material that will
strongly sorb ammonia while exhibiting a decreased
hydrophilicity, preferably a hydrophilicity which is
less than the material's power to absorb ammonia.

25  BRIEF DESCRIPTION OF THE INVENTION

The objects of the present invention have been attained
by hydrophobic tectosilicates that are prepared by a
reaction sequence that comprises removing a substantial
part of the aluminum from the lattice sites of a
30  naturally-occurring or synthetic aluminous tectosilicate
so as to create reactive lattice sites, preferably
hydroxyl-containing nests of general structure $(\equiv SiOH)_4$

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in the silicaceous lattice of the tectosilicate. The
resultant aluminum-deficient tectosilicates are
dehydrated, e.g. by heating them, so as to drive off
water of hydration without destroying or otherwise
5   deactivating the reactive sites. The resultant
materials are then derivatized so as to substitute
selected moieties for the hydroxyl groups, said moieties
being weaker point electric sources than aluminum or,
preferably, than hydroxyl groups. Selection of the
10  appropriate dealumination, dehydration and
derivatization conditions in accord with the present
invention results in the production of a new family of
hydrophobic materials that are microporous, crystalline
and that exhibit a stronger affinity for ammonia than
15  for water under equivalent exposure conditions.

As used herein with respect to a substituent, the term
"weaker point electric source" is defined as possessing
a lower overall charge and/or which charge is
distributed over a larger molecular volume than the
20  charge distribution at, for example: (a) an aluminum
site in an aluminous tectosilicate; (b) a hydroxyl site
formed as a result of aluminum removal.

DETAILED DESCRIPTION OF THE INVENTION

The hydrophobic materials of the present invention are
25  prepared by reacting lattice silyl hydroxyl groups,
preferably those in the tetracoordinate "nest"
configuration, so as to substitute organic moieties,
preferably acyl, alkyl or silyl groups for the hydroxyl
nests. Preferred silyl groups are those of the general
30  formula $Si(R')_n X_p$ wherein n is 0-3, p is (3)-(n), R' is
selected from the group consisting of aryl, alkyl, acyl,
aralkyl, cycloalkyl and mixtures thereof and X is
halogen or an alkoxy group. The preferred acyl, alkoxy
and alkyl groups are lower acyl, alkoxy or alkyl

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radicals such as $C_1$-$C_4$ alkyl, alkoxy or acyl groups,
both branched and straight chain. Preferably n is 1-2
and X is chloro.

The tectosilicates derivatized in this manner are first
5   dealuminated so as to produce the requisite reactive
sites in the silicaceous lattice, preferably by
treatment with aqueous mineral acid. They are then
dehydrated so as to expose these reactive sites.
Although all tectosilicates may include some incidental
10  structural hydroxyl (OH) groups, not enough hydroxyls
are present to allow chemical derivatization to the
extent necessary to impart useful degree of
hydrophobicity. Accordingly, the substrate
tectosilicates must first be treated to increase the
15  number of lattice hydroxyl groups, and should then be
dehydrated to make the hydroxyl groups available for
subsequent chemical derivatization.

The general reaction scheme for the method of this
invention may be depicted as outlined in Figure 1.
20  Replacement of the metal cation (M+) of tectosilicates
by hydronium ion is easily accomplished by exposure of
tectosilicates to aqueous acid. As outlined in Fig. 1,
a Si-O-Al bond of starting material I readily protonates
and dissociates to provide aluminum-associated hydroxyl
25  sites within the lattice as shown by structure II. Kerr
(U.S. Pat. No. 3,682,996) has disclosed the silylation
of type II sites, i.e., by exposure to trimethylsilane
($HSi(CH_3)_3$) to form silylated, aluminum-containing
materials of structure III. Kerr disclosed that type
30  III silylated zeolites absorbed about 40% less
cyclohexane, n-hexane and water than the parent
"hydrogen" zeolites of type II. However, Kerr does not
report any change in selectivity perference.

Aluminous tectosilicates having a silicon to aluminum

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ratio (Si:Al) of greater than about 5 can be almost
totally dealuminated without loss of lattice integrity.
See R.M. Barrer and M.B. Makki, Can. J. Chem., 42, 1481
(1964). This has been accomplished by extended
5   treatment of aluminous tectosiliates with aqueous acid.
Dealumination is thought to afford tectosilicates having
tetracoordinated hydroxylated nests comprising about 4
associated =Si-OH moieties, as depicted in structure IV.
These aluminum-free sites may be termed "exoaluminum
10  sites".

Activated tectosilicate materials both of structures II
and IV would be expected to exhibit reduced
hydrophilicity due to absolute reduction of lattice
charge due to aluminum removal, but would still be
15  expected to sorb water via hydrogen bonding to hydrogen
atoms associated with the remaining aluminum atoms
and/or to the free silyl hydroxyl (SiOH) groups.
Heating aluminum-containing or dealuminated
tectosilicates to relatively low temperatures, i.e., to
20  about 100-200°C, preferably in the presence of a vacuum,
clears pores and channels for absorption by removing
water of hydration from the pores. Exposure of
dealuminated tectosilicates to higher temperatures,
i.e., to about 400-500°C, causes either partial or total
25  destruction of the hydroxyl nests, via dehydroxylation
and formation of new Si-O-Si bonds. N.Y. Chen in J.
Phys. Chem., 80, 60 (1976) has reported that
dealuminized mordenites having Si:Al ratios of greater
than 80 will not absorb water vapor at a pressure of one
30  or 12 mm of mercury.

An early attempt to replace lattice aluminum with
silicon by reaction of the nests with silane was
unsuccessful. See R.M. Barrer and J.-C. Trombe, J.C.S.
Faraday I, 74, 1871 (1978), who also reported the
35  likelihood of some nest silylation to form a

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tectosilicate of structure V (R = SiH$_3$, x < 4). They
also reported that nest hydroxyl groups appeared to be
less reactive to silylation than are the hydroxyl groups
present in structure II of Fig. 1. The hydrophilicity
5   of the silylated tectosilicates was not determined.


The aluminous tectosilicates utilized as starting
materials in the present invention can include
crystalline, amorphous and mixed crystalline amorphous
tectosilicates of natural or synthetic origin or
10  mixtures thereof. The water insoluble crystalline
tectosilicates useful in the present invention are those
that possess interstitial channels of a narrowest
diameter of about 3-13Å. Hereinafter this diameter will
be referred to as pore size. A preferred pore size
15  characterizing the underivatized substrate materials
useful in this invention is about 3-10Å, most preferably
4-8Å. The pore size of any given tectosilicate must be
large enough to admit derivatization materials such as
silanes, alcohols and the like, yet small enough to
20  prohibit entry of unwanted liquid or gas stream
components, i.e., aromatics, ketones, heterocyclic
compounds and the like. Tectosilicates possessing pore
sizes within the range of about 4-13Å readily admit
small gaseous elements and compounds such as water
25  (kinetic diameter [$\sigma$] 2.65Å), carbon monoxide ($\sigma$=
3.76Å), carbon dioxide ($\sigma$= 3.30Å) and ammonia ($\sigma$=
2.60Å).

The most useful aluminous tectosilicate starting
materials preferably will possess a lattice silicon to
30  aluminum ratio of greater than about 5:1.
Tectosilicates having a silicon to aluminum ratio of
less than about five tend to lose their structural
integrity upon dealumination.

An especially preferred class of aluminous tectosilicate

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starting materials is the naturally-occurring
clinoptilolites. These minerals typically have the unit
cell structure:

$$Na_6[(AlO_2)_6(SiO_2)_{30}] \cdot 24H_2O$$
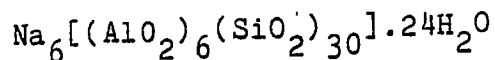
5    wherein the sodium ion content (Na+) may be partially
replaced by calcium, potassium and/or magnesium, etc.
The silicon:aluminum ratio in preferred varieties is
greater than 5 and most preferably greater than about 8.
The pore size is in the range of about 4.0-6.0Å.
10   Clinoptilolite is stable in air to about 700°C and
maintains its structural integrity upon dealumination.

Other naturally-occurring aluminous tectosilicates that
are useful as starting materials are the mordenites,
which typically exhibit the unit cell composition:

15   $$Na_8[(AlO_2)_8(SiO_2)_{40}] \cdot 24H_2O$$
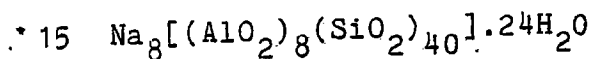
wherein calcium and potassium cations may replace a part
of the sodium cations. The pore size is in the range of
about 3.5-4.5Å. The silicon to aluminum ratio is
generally greater than 5.0 and may be greater than 10 in
20   some samples. Other aluminous tectosilicates such as
ferrierite or erionite would also provide useful
starting materials.

Although naturally-occurring aluminous tectosilicates
are the preferred starting materials due to their low
25   cost and accessibility in large quantities, the
synthetic analogs of the natural tectosilicates and
their derivatives would be of equivalent utility in the
present method. For example, synthetic mordenite
(Zeolon®), available from the Norton Company, would be
30   an acceptable starting material for use in the present
invention. Also, other synthetic, porous tectosilicates

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which have no equivalent in nature could serve as
acceptable starting materials.

The formation of the hydrophobic materials of the
present invention normally will proceed in three steps:

5    (1) dealumination, (2) dehydration and (3)
derivatization with an appropriate alkylating, acylating
or silylating agent.

The dealumination of aluminous tectosilicates with acid
is well known in the art. For example, R.M. Barrer and

10   M.B. Makki in Canadian J. Chem., 42, 1481 (1964)
reported the complete dealumination of clinoptilolite by
refluxing samples in aqueous hydrochloric acid of
varying concentration. In the present method, a strong
acid treatment is preferred, involving exposing

15   pulverized, sieved aluminous tectosilicate to refluxing,
i.e. boiling 2-10N aqueous mineral acid for about 1-3
hours. The preferred acid is about 3-7N hydrochloric
acid, although other strong acids such as sulfuric acid,
nitric acid or phosphoric acid may be useful in some

20   cases.

In some cases, a mild acid treatment involving the
percolation of aqueous acid through a column of crushed
aluminous tectosilicate under ambient conditions has
been found to be satisfactory. Preferably, the

25   tectosilicate starting material will be dealuminated to
a Si:Al ratio of greater than about 25, preferably the
ratio will exceed 100, e.g. about 150-300, and under the
most preferred conditions essentially no lattice
aluminum will be retained, as measured by x-ray

30   fluorescence.

The dealuminated, air-dried tectosilicate materials are
then heated in order to remove most of the pore water of
hydration and to expose the remaining lattice hydroxyl

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groups to derivatization. The heating can be carried
out at any temperature sufficient to effect substantial
dehydration without causing significant lattice
rearrangement and subsequent loss of reactive sites.
5   Typically the dealuminated materials are heated to about
100-200°C for about 10-40 hours, preferably under
reduced pressure. Investigation of the effects of high
temperatures, i.e., of 500-600°C on tectosilicates that
had been subjected to the acid treatment at ambient
10  temperatures indicated that, although substantial
hydrophobicity was exhibited by the samples relative to
the starting materials, the derivatization did not cause
a further increase in hydrophobicity.

Following thermal dehydration at lower temperatures,
15  e.g., about 100-200°C, the dealuminated, dehydrated
materials are allowed to cool and then are exposed to
derivatizing reagents that react so as to functionalize
the internal lattice silyl-hydroxyl groups, the majority
of which are thought to be present in tetracoordinated
20  nests of the unit structure IV, as depicted in Figure 1.
After exposure of the aluminum-free sites ("exoaluminum
sites") to the derivatizing reagent, the nest sites will
contain from about 1-4 [ Si-OR] units wherein R is
alkyl, acyl, or silyl substituted with 1-3 halogen,
25  alkoxy alkyl, aryl, aralkyl or cycloalkyl substituents
wherein the alkyl, alkoxy or acyl groups, either
directly attached to the lattice silyloxy or bound to
the silicon atom of the R group, preferably are $C_1$-$C_4$
alkyl, alkoxy or acyl groups.

30  Reagents (RX) useful to replace the hydrogen atom of the
nest silyl-hydroxyl groups with the substituent R
include a wide range of the reagents known in organic
chemistry to be useful to alkylate, acylate or silylate
hydroxyl groups. Such agents are generally disclosed by
35  I.T. Harrison et al. in Compendium of Organic Synthetic

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_Methods_, Wiley-Interscience, N.Y. (1971) at pages 124-
131, the disclosure of which is incorporated by
reference herein.  Preferred reagents include the
lower-$C_1$-$C_4$-alkanols or $C_1$-$C_4$ alkyl halides such as
5  methanol, ethanol and the like or methyl chloride,
methyl iodide, ethyl chloride, butyl bromide and the
like.  Lower-$C_1$-$C_4$-alkanols have been found to be
especially effective as derivatizing agents when
thermally reacted with the tectosilicates under pressure
10  either neat or in the presence of catalysts.  Other
useful alkylating reagents include the $C_1$-$C_4$-diazo-
alkanes.

Nest hydroxyl groups may be acylated by exposure to
ketenes such as ketene itself or to alkyl or dialkyl
15  ketenes such as dimethylketene.  Reaction of a silyl-
hydroxyl group with ketene affords an SiOR moiety
wherein R is acetyl, while reaction with dimethylketene
introduces R as dimethylacetyl.

A wide variety of silylation reagents may be used to
20  introduce substituted silyl substituents into the
tectosilicate nests, i.e., to introduce R as $[Si(R')_n X_p]$
wherein n is 0-3, p is (3)-(n), R' is selected from the
group consisting of $C_1$-$C_4$ lower alkyl, $C_5$-$C_7$ cycloalkyl,
aryl, $C_1$-$C_4$-acyl, aralkyl and mixtures thereof; and X is
25  a halogen atom, i.e., Cl, F, I, Br or mixtures thereof,
or a (lower) alkoxy group.

Di-, tri- or tetrafunctional silylation reagents may
also react with 2-4  =Si-OH groups in a single nest to
functionally replace the missing aluminum atom with the
30  bridging unit SiR'q, wherein q is 0-2, thus bridging the
aluminum-deficient site with 1-2 silicon atoms.  This
reaction would occur via the elimination of 2-4 HX
groups and the formation of O-Si-O bridges.  For
example, when dimethyldichlorosilane is reacted with

lattice silyl hydroxyl groups[13] ($\equiv$Si-OH), structural units
such as $\equiv$SiOSi(CH$_3$)$_2$Cl or $\equiv$SiOSi(CH$_3$)$_2$OSi may be
introduced into the nests. Of course, the methyl groups
may be replaced with any of the groups represented by R'

5  and Cl may be replaced by another halogen atom or by an
alkoxy group.

Typical monofunctional silylating reagents which
introduce Si(R')$_3$ units include trimethylchlorosilane,
trimethylfluorosilane, dimethyliso-propyl-chloro-silane

10 and the like. Preferred difunctional silylating agents
include the dihalodialkylsilanes, e.g.,
dichlorodimethylsilane and the dialkoxy(dialkyl)silanes,
e.g, diethoxydimethylsilane. Tri- and tetrafunctional
silanes may also be employed to derivatize the

15 tectosilicates of the present invention, such as silicon
tetrafluoride, tetrachlorosilane, and
trifluoromethylsilane.

Reaction of the dealuminated, dehydrated tectosilicates
with the silylation reagent may be carried out by

20 contacting the materials with the reagent in the liquid
or gas phase. Preferably, an excess of silylation
reagent in a suitable solvent is slurried with the
tectosilicate. Heating and/or added catalysts may be
employed if necessary, depending on the reactivity of

25 the tectosilicate and the silane.

Gaseous hexamethyldisilazane can be reacted with lattice
hydroxyl groups to introduce trimethylsilyl groups into
the nests, following the procedure of Fenimore et al.,
Anal. Chem., 48, 2289 (1976), the disclosure of which is

30 incorporated herein by reference.

The methods of the present invention readily afford
hydrophobic microporous, crystalline silaceous materials
which exhibit a greatly reduced affinity for water while

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maintaining high affinities for less polar molecules
such as ammonia. The hydrophobicity or reduction in
hydrophilicity of a tectosilicate can be quantitated in
terms of its absorption of water per unit of

5   tectosilicate under a given set of exposure conditions
(retention volume). That any observed reduction in
water retention is due to hydrophobicity as opposed to a
general reduction in retention can be established by
measuring the retention of a similarly-sized molecule of

10  comparable or lesser polarity, such as ammonia,
nitrogen, methane or carbon dioxide. By the use of
these general techniques, the derivatization methods of
the present invention provide microporous crystalline
silaceous materials that exhibit an affinity for water

15  vapor as measured in terms of retention (ml of $H_2O$/g of
material at STP), which is reduced an additional 10-50%,
preferably about 15-45% under the absorption capacity
observed prior to the derivatization step but after the
tectosilicates have been acid treated and activated

20  toward derivatization by heating. When ammonia vapor
retention is used as a reference, the absorption of
water vapor into the derivatized material is no more
than about 20-80% that of ammonia and is probably much
less. In contrast, both ammonia and water are

25  irreversibly absorbed on heat dehydrated or hydrated
tectosilicate samples which have not been treated with
acid or derivatized, exhibiting retention volumes of
greater than 200 ml of vapor per column-gram of
aluminous tectosilicate under the gas-solid

30  chromatography conditions used to measure the retention
volumes.


The invention will be further illustrated by reference
to the following examples.


The following six procedures were used to modify the
35  properties of clinoptilolite (Hector, Cal., NL

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Industries).

## PROCEDURE A1 - MILD ACID WASH

The tectosilicate, i.e., clinoptilolite, was crushed in
a jaw crusher, then pulverized in a Braun Pulverizer.
5    The pulverized material was passed through a 50-100 mesh
RoTap® sieve agitator and used to fill a 2-inch
diameter, 3-foot long Pyrex® tube two-thirds full. The
powdered material was held in place with a glass wool
plug.  Forty liters of hydrochloric acid (6N) were
10   flowed through the packed column at a rate of about 9
ml/min. at 27°C.  The acid-treated material was washed
by flushing with three column volumes of distilled
water, then air-dried. Clinoptilolite (Hector, Cal.)
treated in this manner was light green and exhibits a
15   Si:Al ratio of approximately 30.

## PROCEDURE A2 - STRONG ACID WASH

The light green material (225 g) isolated from procedure
A1 was placed in a 4.0 liter round bottomed flask and
2.0 l of 6N HCl was added.  The slurry was heated at
20   reflux for 2.0 hours.  A white mineral was recovered by
vacuum filtration and washed repeatedly with deionized
water.  The Si:Al ratio of clinoptilolite treated in
this manner was about 212.

## PROCEDURE H1 - MILD HEAT TREATMENT

25   About 10 g of pulverized tectosilicate (clinoptilolite)
was placed in a 250 ml beaker and heated to 150°C for 20
hours in a vacuum drying oven at less than 10 mm Hg.
After vacuum heating, the material was stored at 150°C
at  ambient pressure.

30   PROCEDURE H2 - HIGH HEAT TREATMENT

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About 10 g of pulverized tectosilicate (clinoptilolite)
was placed in a quartz 250 ml beaker and heated at 550°C
for 14 hours at ambient pressure, then transferred to a
150°C oven for storage at ambient pressure.

5  PROCEDURE D1 - SILYLATION

Pyridine was allowed to stand over potassium hydroxide
pellets for 24 hours, then distilled from barium oxide
and stored over 4A molecular sieves.  Toluene was
refluxed over sodium metal for three days, then
10  distilled and stored over Linde type 4A molecular
sieves.  A reagent mixture of 20% pyridine, 15%
dichlorodimethylsilane and 65% toluene was prepared and
stored over the molecular sieves.

A 250 ml round bottomed flask equipped with magnetic
15  stirring, a reflux condenser and an argon inlet was
flushed with dry argon and charged with 10 g of
pulverized tectosilicate followed by addition of 100 ml
of the reagent mixture described hereinabove.  The
resultant slurry was refluxed for 20 hours.  After
20  reaction, the acid-treated tectosilicate material was
isolated by filtration and washed with dry toluene and
methanol.  The material was refluxed for at least two
hours in methanol, recovered by filtration and stored
under ambient conditions.

25  PROCEDURE D2 - METHYLATION

About 5.0 g of pulverized material was placed in a steel
bomb with about 50 ml of methanol.  The bomb was sealed
and heated to 220°C for 4-12 hours.  The bomb was cooled
to 25°C and the material recovered by filtration.

30  DETERMINATION OF GAS RETENTION VOLUMES

The treated, pulverized tectosilicate was vacuum-packed
into a silylated glass column (0.125 inch inner
diameter, 0.25 inch outer diameter) and held in by plugs
of silylated glass wool. The column was inserted into
5 the oven of a gas chromatograph. The injector port was
maintained at 200°C, the detector oven at 250°C and the
column maintained at an initial conditioning temperature
of 45-50°C for 10-30 minutes. The detector filament
current was held at 150mA and the carrier gas (He) inlet
10 pressure was 60 psi. Gas injections (75-125 μl) were
made at 4-7 psi above ambient pressure and liquid
injections were of 1-2 μl. Water and ammonia retention
volumes were measured at a column temperature of 200°C.
Under these conditions, ammonia was irreversibly
15 absorbed. Results were expressed as K (ml of gas
absorbed/g of absorbent at STP).

The properties of a number of modified Hector,
California clinoptilolites prepared by various
combinations of the procedures described above are
20 summarized in Table I. In all cases the procedures were
performed or .omitted in the order indicated. The
silicon:aluminum ratios were determined by energy-
dispersive x-ray spectrometry (Tracor Spectrace model
440, Tracor-Northern 2000 Analyzer) with data reduction
25 accomplished using the program Super ML, Tracor X-Ray,
Inc.

TABLE I

| Ex. | Treatment | $K(H_2O)$ 1 | Si/Al | Total Carbon Analysis (%)[4] |
|-----|-----------|-------------|-------|------------------------------|
| 1   | none      | >200        | 10.00 | 0.28                         |
| 2   | $A_2H_1D_2$ | 21        | High[2] | 0.69                       |

| | | $^{18}$ | | |
|---|---|---|---|---|
| 3 | $A_2H_1D_1$ | 27 | High[2] | 0.62 |
| 4 | $A_2H_1D_0$ | 36 | 211.67 | 0.12 |
| 5 | $A_1H_1D_2$ | 58 | 39.58 | 0.52 |
| 6 | $A_1H_2D_0$ | 59 | 6.93[3] | 0.30 |
| 7 | $A_1H_2D_1$ | 64 | 32.66 | 0.63 |
| 8 | $A_1H_1D_1$ | 79 | 33.00 | 2.37 |
| 9 | $A_1H_1D_0$ | 93 | 34.43 | 0.38 |
| 10 | $A_1H_0D_2$ | 129 | 33.56 | 0.29 |
| 11 | $A_1H_0D_0$ | >200 | 10.82[3] | N.T. |
| 12 | $A_1H_0D_1$ | >250 | 39.01 | 2.90 |
| 13 | $A_1H_2D_2$ | >570 | 6.8[3] | 0.36 |

1  ml/g at STP; K(NH3) was >200 in all cases.

2  Lattice Al not detected in these materials.

3  Anomalous results probably due to operator error.

4  Galbraith Laboratories, Inc., Knoxville, Tenn.

From the results tabulated on Table I it can be
generally seen that combinations of mild or strong acid
washes followed by high or low temperature heating
significantly increases the hydrophobicity of the
tectosilicate even without a further derivatization
step.  The effect is most pronounced in the case of
samples washed with strong acid, then heated at 150°C

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($A_2H_1D_0$ Ex. 4). However, examples 3 and 2 demonstrate
that a further significant increase in hydrophobicity
can be attained by silylation or methylation,
respectively, of this material. The total percent
5  carbon is also increased in these samples by over 400%
in each case. Likewise, an increase in hydrophobicity
is observed in the case of the silylation (Ex. 8) or
methylation (Ex. 5) of the material of Ex. 9, which had
been subjected to the mild acid wash and then to 150°C
10 heating. The greater affinity for water observed for
these materials as opposed to the materials of examples
3 and 2 is thought to reflect the presence of more
reactive sites, i.e., silyl nests, in the latter two
materials, which had been exposed to stronger
15 dealumination conditions.

However, examples 7 and 13 indicate that no increase in
hydrophobicity was observed for the material of Ex. 6
when derivatization was attempted; rather, a decrease
was observed. It is thought that the failure of
20 derivatization to affect the observed hydrophobicity in
the case of the material of Ex. 6 is due to the collapse
of hydroxyl nests or other reactive sites formed by the
initial acid wash. Furthermore, a comparison of Example
pairs 8 and 7, 9 and 6 indicates that, for otherwise
25 equivalently-prepared samples, a high heat treatment
(H2) results in a significantly lower carbon
incorporation when either methylation or silylation is
attempted. This provides further support for a
mechanism involving the production and preservation of
30 activated nests following the strong acid, mild heat
treatment combination. The attempted silylation (Ex. 12)
of material which had been acid washed but not
dehydrated (by heat) failed to increase the
hydrophobicity of the material of Ex. 11, possibly due
35 to the blockage of reactive sites by water of hydration.
Methylation of the same material caused a moderate

increase in hydrophobicity (Ex. 10).

The hydrophobic derivatized materials of Exs. 3 and 2
also possessed no detectable lattice aluminum by x-ray
fluoroscopy, a negative result also expected and
5     observed in the case of Silicalite® (Union Carbide).
This provides confirmation that the strong acid wash
conditions are effective to remove lattice aluminum and
produce reactive hydroxyl-containing nests that are
available for derivatization.  Although removal of
10    lattice aluminum is, by itself, adequate to
significantly increase the hydrophobicity of the
clinoptilolite, and, in fact, is the major contributor
to the hydrophobic properties involved, it is apparent
from Examples 8, 3, 5 and 2 that the hydrophobic
15    properties are optimized, for this set of treatment
variables, by further silylation or methylation.
Significant hydrophobic affects are generally observed
in both derivatized and underivatized materials when the
Si:Al ratio exceeds about 25.

20    The hydrophobic materials prepared according to examples
8, 3, 5 and 2 would be expected to absorb significant
amounts of ammonia from wet human or animal excreta, and
to do so more effectively than any material employed
heretofore, such as underivatized tectosilicates,
25    phyllosilicate clays, silica gel and the like.  To this
end, the new materials may be incorporated in diapers,
bedpads and the like, either in vapor- or moisture-
permeable compartments or distributed throughout the
textile matrix.  For example, in the case of a bedpad or
30    disposable diaper which typically consists of an
absorbent core of natural or synthetic fibers, a
permeable top or inner sheet and a liquid-impervious
back or outer sheet, an effective amount of the new
material of the instant invention can be incorporated in
35    the absorbent core of the disposable diaper.  The amount

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of ammonia-absorbent used can vary from about 1% to 50%,
preferably about 15% to 25% (based on the weight of the
diaper), depending on whether the diaper is intended for
day or night use; and on the age of the user.

5    Additionally, an effective amount of the new material
may be solution-coated onto a disposable diaper top
sheet, incorporated into the absorbent lining of plastic
baby pants or incorporated into cloth diapers by known
methods in the art of dispersing particulate solids into
10   fibrous substrates.

The new hydrophobic materials of this invention may also
be employed as animal litter, preferably when aggregated
into pellets, either alone or in combination with other
absorbent materials.  Typical animal litter consists of
15   absorbent inorganic or organic materials such as
attapulgite, vermiculite and calcium montmorillonite
(i.e., clay), agglomerated wood dust, wood chips,
dehydrated grasses, straw, or alfalfa, fly ash and the
like.  The addition of an effective amount, e.g. about
20   5-95%, preferably about 20% to 30% or more (based on
total litter weight) of the new material to these
litters will enhance the deodorizing capabilities of the
litter without substantially reducing the litter
absorbent characteristics.

25   The new hydrophobic materials of this invention may also
be used in filter cartridges in pipes, cigars or
cigarettes, either alone or dispersed throughout and/or
deposited on conventional tobacco smoke filtration
materials.  Used in this capacity, effective amounts of
30   the new hydrophobic materials would be expected to
absorb significant amounts of carbon monoxide from the
mainstream smoke more effectively than hydrophilic
materials commonly used in smoke filters such as
cellulose, activated carbon, naturally-occurring or
35   synthetic aluminous tectosilicates and the like.  For

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example, a filter can be made having a section
consisting of about 10-75 mg, preferably about 40 to 50
mg of the new hydrophobic material either front of or
behind the standard filter material. Additionally,
5   about 10-40 mg, preferably about 20 to 30 mg of the new
material may be incorporated in the standard filter
material itself. Likewise, effective amounts of the
powdered materials of this invention could be
incorporated into wrapping materials such as paper and
10  tobacco leaf used to shape cigarettes or cigars in order
to reduce the carbon monoxide in the sidestream smoke of
the burning cigar or cigarette. The amount used will
depend upon the total weight, volume and composition of
the wrapping material used.


15  While certain representative embodiments of the
invention have been described herein for purposes of
illustration, it will be apparent to those skilled in
the art that modifications therein may be made without
departing from the spirit and scope of the invention.

WE CLAIM:

1. A hydrophobic microporous crystalline tectosilicate
   material of regular geometry comprising aluminum-
   free sites in a silaceous lattice that are
5  characterized by the presence of about 1-4
   associated moieties of the formula $\equiv$SiOR wherein R
   is a substituent that is a weaker point electric
   source than aluminum.

2. The material of claim 1 wherein R is a substituent
10 that is a weaker point electric source than a
   hydroxyl group.

3. The material of claim 2 wherein R is a substituent
   selected from the group consisting of $C_1$-$C_4$ alkyl,
   $C_1$-$C_4$ acyl, and $SiR'_n X_p$ wherein R' is selected from
15 the group consisting of $C_1$-$C_4$-alkyl, cycloalkyl,
   aryl, $C_1$-$C_4$-acyl, aralkyl and mixtures thereof, X
   is a halogen atom or a (lower)-alkoxy group, n is
   0-3 and p is (3)-(n).

4. The material of claim 2 wherein the aluminum-free
20 site is bridged by 1-2 of the units $SiR'_q$ wherein q
   is 0-2, and wherein R' is selected from the group
   consisting of C1-C4 -alkyl, cycloalkyl, aryl, C1-C4
   acyl, aralkyl and mixtures thereof.

5. The material of claim 3 or 4 wherein said sites are
25 created by a process comprising removing aluminum
   from an  aluminous tectosilicate lattice.

6. The material of claim 5 wherein R is $C_1$-$C_4$ lower
   alkyl or $SiR'_n Cl$ wherein R' is $C_1$-$C_4$ alkyl and n is
   1-2.

30 7. The material of claim 5 wherein the lattice Si:Al

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ratio after aluminum removal is greater than about
25.

8.  The material of claim 7 wherein the lattice is
essentially aluminum-free.

5    9.  The material of claim 1 which exhibits an
absorption of water vapor which is no more than
about 20-80% the absorption of ammonia vapor.

10.  A method for preparing a hydrophobic microporous
crystalline material of regular geometry
10       comprising:
(a)  creating aluminum-deficient sites in the
lattice of a natural or synthetic aluminous
tectosilicate starting material, said sites
being characterized by the presence of about 4
15       associated $\equiv$SiOH moieties;
(b)  heating the aluminum-deficient tectosilicate
to remove water of hydration;
(c)  reacting the $\equiv$Si-OH moieties with a
derivatizing reagent whereby about 1-4 of said
20       moieties per site are converted to a moiety of
the formula $\equiv$SiOR wherein R is a substituent
which is a weaker point electric source than
aluminum.

11.  The method of claim 10 wherein R is a substituent
25       selected from the group consisting of $C_1$-$C_4$ alkyl,
$C_1$-$C_4$ acyl and $SiR'_n X_p$ wherein R' is selected from
the group consisting of cycloalkyl, aryl, acyl,
alkyl, aralkyl and mixtures thereof, X is halo or
(lower)alkoxy, n is 0-2 and p is (3)-(n), or
30       whereby 2-4 of the  Si-OH moieties are bridged by
the unit $SiR'_q$ wherein q is 0-2.

12.  The method of claim 11 wherein reaction of two of

the $\equiv$Si-OH moieties with the derivatizing agent
results in the elimination of two HX molecules and
the bridging of the moieties by the unit $-SiR_2-$.

5      13.  The method of claim 11 wherein R is $C_1-C_4$ alkyl or
            R' is $C_1-C_4$ alkyl, n is 1-2 and X is chloro.

       14.  The method of claim 10 wherein the Si:Al ratio of
            the starting material is greater than about 5:1.

       15.  The method of claim 11 wherein the aluminum
            deficient sites are created by exposure of the
10          aluminous tectosilicate to aqueous mineral acid.

       16.  The method of claim 15 comprising removing
            essentially all of the aluminum from the aluminous
            tectosilicate lattice.

       17.  A method for decreasing the hydrophilicity of a
15          tectosilicate material comprising:
            (a)  removing a substantial portion of the aluminum
                 from the lattice sites of an aluminous
                 tectosilicate to create aluminum deficient
                 sites characterized by about 4 associated
20               $\equiv$SiOH moieties;
            (b)  dehydrating the aluminum-deficient
                 tectosilicate at a temperature at which the
                 integrity of the lattice is retained; and
            (c)  reacting the $\equiv$SiOH moieties with a
25               derivatizing reagent selected from the group
                 consisting of dihalodialkylsilanes,
                 dialkoxydialkylsilanes, $C_1-C_4$-alkanols and
                 $C_1-C_4$ alkylhalides whereby about 1-4 of said
                 moieties per site are converted to a moiety of
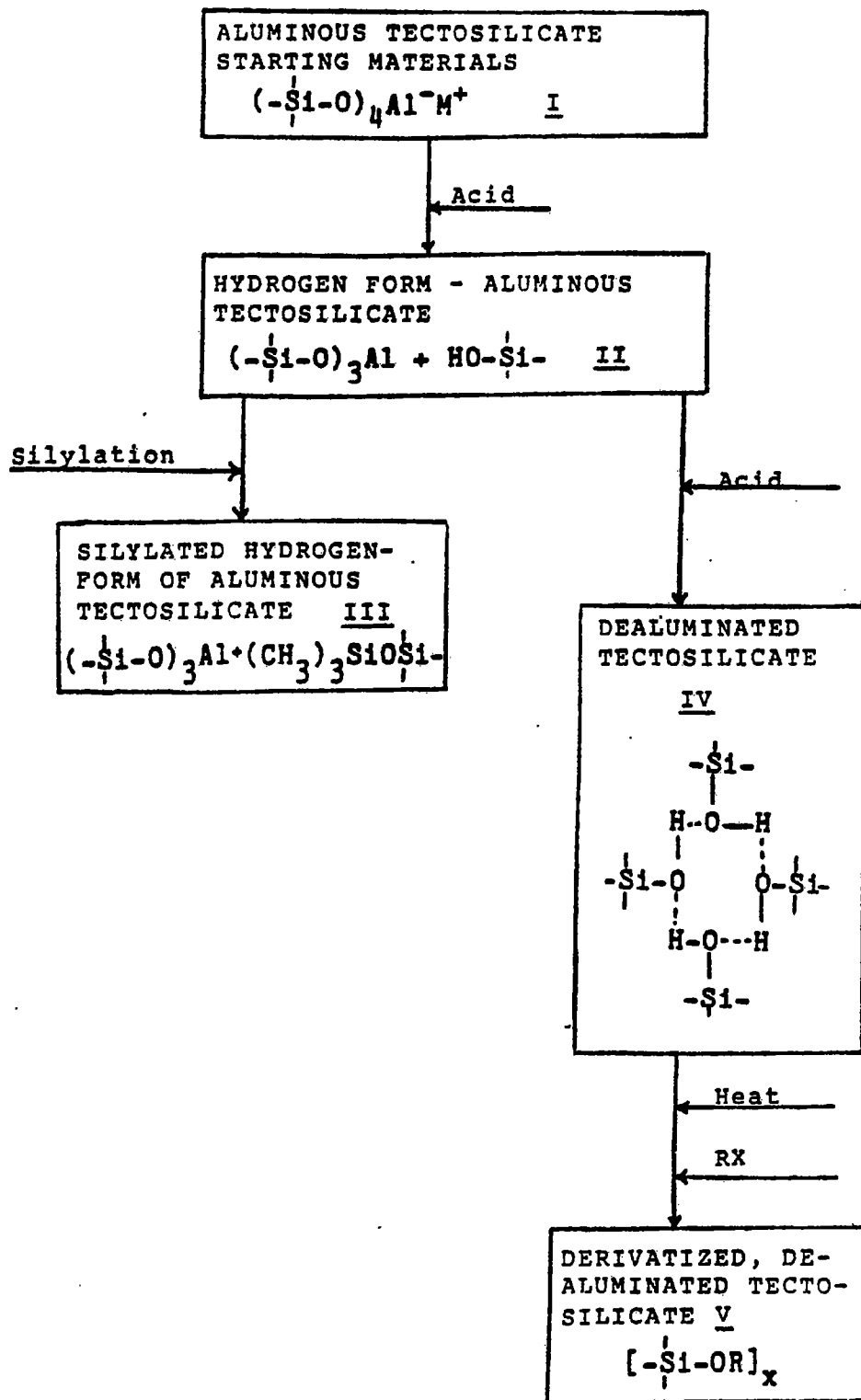30               the formula:

            $\equiv$SiOR
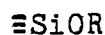
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wherein R is selected from the group
consisting of $C_1$-$C_4$ alkyl or $SiR_2X$ wherein X
is a halogen atom; or whereby at least two
≡SiOH moieties per site are bridged by the
5       unit $SiR'_q$ wherein q is 0-2.

18.   The method of claim 17 wherein the derivatizing
      agent is dichlorodimethylsilane or methanol.

19.   The method of claim 17 wherein the starting
      material is a clinoptilolite.

10  20.   A diaper comprising an absorbent inner core which
          comprises an effective amount of the material of
          claim 1.

21.   A bedpad comprising an absorbent inner core which
      comprises an effective amount of the material of
15        claim 1.

22.   Animal litter comprising an effective amount of the
      material of claim 1.

23.   A cigarette or pipe filter comprising the
      hydrophobic material of claim 1.

20  24.   The filter of claim 23 comprising about 40-50 mg of
          the hydrophobic material.

25.   A cigarette or cigar wrapping comprising the
      material of claim 1.

FIG 1. DERIVATIZATION OF TECTOSILICATES

ALUMINOUS TECTOSILICATE
STARTING MATERIALS

$(-\overset{|}{\underset{|}{Si}}-O)_4 Al^- M^+$      $\underline{I}$

↓ Acid

HYDROGEN FORM - ALUMINOUS
TECTOSILICATE

$(-\overset{|}{\underset{|}{Si}}-O)_3 Al + HO-\overset{|}{\underset{|}{Si}}-$   $\underline{II}$

Silylation →

← Acid

SILYLATED HYDROGEN-
FORM OF ALUMINOUS
TECTOSILICATE   $\underline{III}$

$(-\overset{|}{\underset{|}{Si}}-O)_3 Al + (CH_3)_3 SiO\overset{|}{\underset{|}{Si}}-$

DEALUMINATED
TECTOSILICATE

$\underline{IV}$

$-\overset{|}{\underset{|}{Si}}-$

H--O—H

$-\overset{|}{\underset{|}{Si}}-O$      $O-\overset{|}{\underset{|}{Si}}-$

H-O---H

$-\overset{|}{\underset{|}{Si}}-$

↓ Heat

RX

DERIVATIZED, DE-
ALUMINATED TECTO-
SILICATE $\underline{V}$

$[-\overset{|}{\underset{|}{Si}}-OR]_x$

# INTERNATIONAL SEARCH REPORT

International Application No  PCT/US84/02087

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 3

According to International Patent Classification (IPC) or to both National Classification and IPC

Int Cl 3 C07F  7/02
US Cl  260/448R

## II. FIELDS SEARCHED

### Minimum Documentation Searched 4

| Classification System | Classification Symbols |
|---|---|
| US | 260/448R<br>131/331<br>604/360 |

### Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 5

## III. DOCUMENTS CONSIDERED TO BE RELEVANT 14

| Category * | Citation of Document, 16 with indication, where appropriate, of the relevant passages 17 | | Relevant to Claim No. 18 |
|---|---|---|---|
| A | US, A, 2,911,386 | 03 November 1959<br>OLSON et al | 1-25 |
| A | US, A, 3,488,368 | 06 January 1970<br>SPIVACK | 1-25 |
| A | US, A, 3,507,897 | 21 April 1970<br>KANNER et al | 1-25 |
| A | US, A, 4,151,189 | 24 April 1979<br>RUBIN et al | 1-25 |
| A | US, A, 4,157,978 | 12 June 1979<br>LLENADO | 1-25 |

* Special categories of cited documents: 15

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV. CERTIFICATION

| Date of the Actual Completion of the International Search 2 | Date of Mailing of this International Search Report 2 |
|---|---|
| 06 March 1985 | 1 2 MAR 1985 |
| International Searching Authority 1 | Signature of Authorized Officer 20 |
| ISA/US | V. Miller   Vincent Mill |

Form PCT/ISA/210 (second sheet) (October 1981)